Transmission Electron Microscopy of Plutonium Alloys

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Until the 1950s, direct observation of microstructures was limited by the wavelength of light to resolutions of some fraction of a micrometer, even under the best of circumstances. With the advent of transmission electronmicroscopy (TEM), in which electrons rather than light are used to image microstructural features, the resolution reached a nanometer. Today, we can image those features with near-atomic-scale resolution. These developments have revolutionized the study of defects and microstructures, which has led to a better understanding of material properties.

Plutonium Proves to Be Most Difficult for TEM

TEM samples must be thin enough to allow the electron beam to penetrate and probe the structure. For most materials, the samples can be made into foils only a few thousand angstroms thick by chemical thinning or ion milling. Because of its high atomic number, however, plutonium foils must be thinner than those of most other metals or alloys. In addition, because of the radioactive and hazardous nature of plutonium, samples must be prepared in glove boxes, and the sample loading must be carefully carried out so as to minimize contamination of the electron-microscope chamber and its surroundings during examination.

However, the most difficult aspect of preparing plutonium for TEM measurements is its extremely reactive nature. Even in very dry air, the plutonium surface will immediately oxidize to plutonium dioxide. Clearly, the key to successful preparation of TEM specimens of plutonium metal is to minimize the surface oxidation. Plutonium samples have been successfully prepared with standard TEM electropolishing techniques, although preparing the thin foil is typically a struggle. We prepared suitable foils by rapidly transferring the prepared samples into an inert environment such as a liquid medium or vacuum (Zocco and Rohr 1988), thus minimizing the time the samples were exposed to the atmosphere.

For our plutonium observations, we used a JEOL 2000EX microscope. An accelerating voltage of 200,000 volts produces a highly penetrating electron beam that enables us to examine plutonium samples. I will briefly describe results of the few TEM examinations conducted at Los Alamos. Ours was the only work of this kind until very recently, when Adam Schwartz and Mark Wall began TEM studies of plutonium at Lawrence Livermore National Laboratory (private communication).

Direct Observation of Martensite in Pu-Ga Alloy

TEM has become an indispensable tool to study mechanisms of phase transformations, especially the crystallographic relationship between the parent and product phases. For the first time, Zocco et al. (1990) were able to confirm the martensitic nature of the transformation from δ-stabilized Pu-Ga alloys to monoclinic α′ (for a discussion of phase transformations in plutonium, see the article "Plutonium and Its Alloys" on page 290). The α′–martensite platelets in δ-grains are shown in Figure 1(a). During the transformation, the change in shape must be accommodated in the product and the parent phases. Indeed, we were able to demonstrate that the α′–martensite platelets twin internally along the

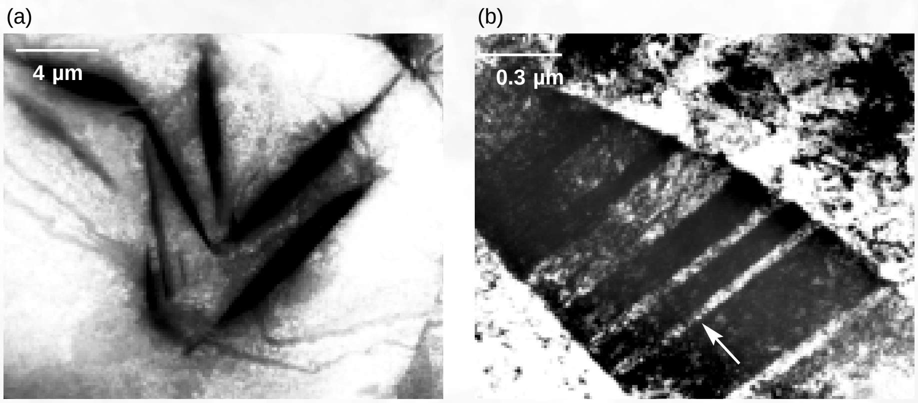

Figure 1. Direct Observation of Martensites in Pu-Ga Alloy
(a) A TEM image shows α′-plates (dark phase) inside the δ-phase of a Pu–3.4 at. % Ga alloy. The sample was cooled to low temperature to transform martensitically to the monoclinic α′-phase. Note the crystallographically distinct orientations of the martensite plates. (b) At higher magnification, twin boundaries (one perpendicular to arrow) can be seen within an individual plate.
(This figure was reproduced courtesy of *Acta Metall. Mater.*)

(205) planes to make this accommodation, as shown in Figure 1(b).

With the aid of selected-area electron diffraction, we were also able to identify the crystallographic relationship between the α′- and the δ-phase. The close-packed $(111)_\delta$ planes were nearly parallel to the closest-packed $(020)_\alpha$ planes in the α′-phase. The habit plane was found to be near the $(132)_\alpha$ plane. These results were consistent with the predictions based on crystallographic theories of martensite formation (Adler et al. 1986). As Hecker pointed out (page 328), to solve some of the remaining mysteries surrounding phase transformations in plutonium alloys, we should be able to apply TEM routinely in the study of those transformations.

Helium Bubbles in Plutonium

The need to extend the lifetime of plutonium pits and concerns over the long-term storage of excess plutonium have refocused attention on self-irradiation damage of plutonium and its alloys. One of the most intriguing puzzles about aged plutonium is what happens to the 40 parts per million by weight per year of helium that are grown into the plutonium lattice as a result of α-particle radioactive decay. Specifically, will helium bubbles form during long-term plutonium storage or will the helium help to initiate void swelling as plutonium ages? (For a full discussion, see the article "Radiation Effects in Plutonium" on page 274.)

Helium is not expected to be very mobile at room temperature. To allow it to move, we intentionally annealed a 21-year Pu-Ga alloy sample at 400°C for one hour. Under those conditions, the helium did indeed move and agglomerate, as first shown at Los Alamos by Rohr et al. (1984). We subsequently showed that very fine bubbles formed in the grain interiors and larger bubbles formed in the grain boundaries, as shown in Figure 2. These techniques must now be applied to the study of all facets of self-irradiation damage—helium generation, void swelling, and lattice damage.

Nanoscale Structures in Plutonium

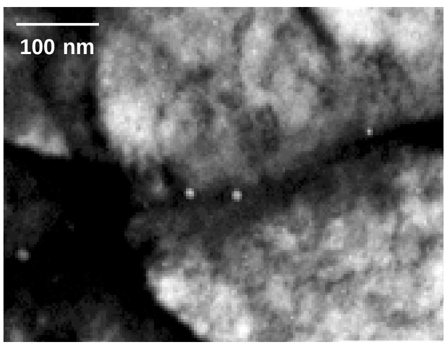

Figure 2. Helium Bubbles in Plutonium

After heating a 21-year Pu-Ga alloy sample at 400°C for one hour, we observed helium bubbles along the grain boundaries. A significant number of bubbles were seen inside grains as well.

(This figure was reproduced courtesy of the Materials Research Society.)

Like many other metals, plutonium can be deposited onto substrates by vapor-deposition processes (for example, magnetron sputtering). Such deposition processes are often used to synthesize very fine grained microstructures or to retain metastable phases. Structures at the nanoscale level are of great interest because they offer new avenues for tailoring materials according to very special properties that are needed. They also provide new avenues for studying the fundamental properties of materials.

We have examined thin foils of triode sputter-deposited Pu-Ga alloys fabricated by Harry Rizzo at Lawrence Livermore National Laboratory. These foils exhibited an extremely fine grain structure, as shown in Figure 3. Some grains were as small as 100 nanometers. In addition, sputter deposition often produced multiphase structures, including α- + β-phase mixtures. We used electron diffraction analysis to identify the (201) plane, a twin plane in the α-phase (Zocco et al. 1989), in contrast to the (205) plane found in the α'-martensite. TEM is an indispensable tool for characterizing such materials.

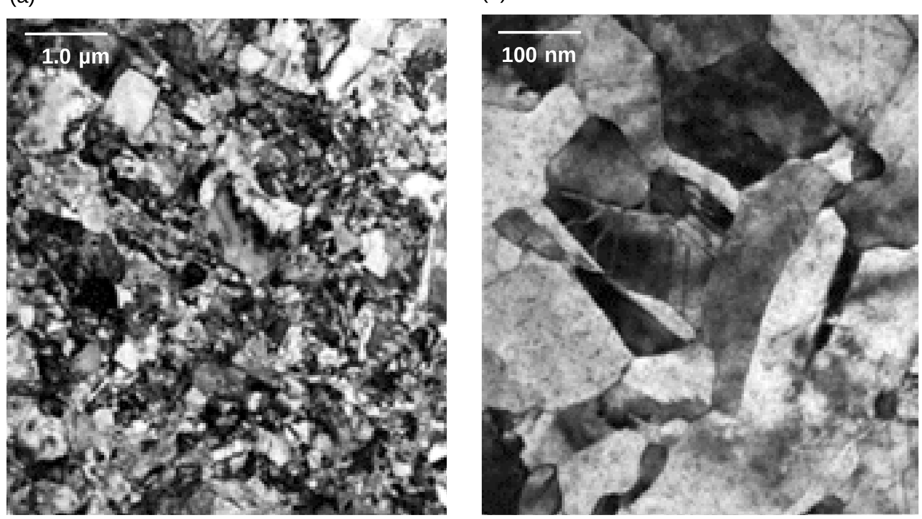

Figure 3. Nanoscale Structures in Plutonium

(a) A sample showing the fine-grained, two-phase α + β Pu-Ga alloy made by sputter deposition. (b) At higher magnification, the sample is seen to have extremely fine grains and some substructure—twin boundaries, stacking faults, and dislocations.

Summary

TEM has helped us understand the unusual properties of and physical phenomena in plutonium and its alloys. Los Alamos paved the way for the use of this technique many years ago. Unfortunately, however, further development of TEM stopped during the 1990s. Only now are we reviving this capability at Los Alamos and Lawrence Livermore National Laboratories. Indeed, it is imperative that we turn TEM into a routine investigative tool for the study of plutonium metallurgy and interfaces. We must investigate the latest TEM capabilities that yield resolution near the atomic level, which would allow us to do analytical electron microscopy (for chemical analysis at the microlevel) to help us in deciphering the mysteries of plutonium. ■

Further Reading

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Thomas Zocco received his B.S. (1982) and M.S. (1984) degrees in materials science and engineering from the University of Utah. In 1984, Tom joined the Laboratory as a technical staff member in the Plutonium Metallurgy Group of the Materials Science and Technology Division. He was originally tasked to provide transmission electron microscopy analyses to several programs, including irradiated materials for fusion reactors and optical coatings for laser mirror applications. Over the last 16 years, Tom investigated the microstructural and crystallographic characteristics of many materials—from fossilized dinosaur bones to plutonium metal and alloys. Tom is an active member of the Science Leadership Council of the Nuclear Materials Technology Division and has authored and coauthored over 60 scientific journal and Laboratory publications.